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N-Heterocyclic Olefin Stabilized Boron Dication

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Boron mono- and di-cations featuring nucleophilic *N*-heterocyclic olefin and pentamethylcyclopentadienyl substituent have been prepared and structurally characterized. Experimental and theoretical investigations show that [η^5-Cp*B-NHO]$^{2+}$ is considerably more Lewis acidic than [η^5-Cp*B-IMes]$^{2+}$ due to steric congestion imposed by the bent geometry of NHO around the central boron atom.

Tri-coordinate boron species have been the focal point of recent research interests due to their potential applications in optoelectronic devices and organic synthesis. One of the latest developments focuses on the Frustrated Lewis Pair activation of small molecules.[1-5] In addition to the highly fluorinated boranes, introduction of positive charge at the boron centre can also effectively increase the reactivity of the molecule.[6-11] Studies have shown that carbene-stabilized dialkylborenium cations indeed catalysed hydrogenation of imine and electro-oxidation of H_2.[12-15] In an attempt to increase the electron deficiency of boron cations, several boron di- and tri-cations have also been synthesized and structurally characterized in the past few years.[16-23] Selected boron cations that feature carbon-based ligands are shown in Figure 1.

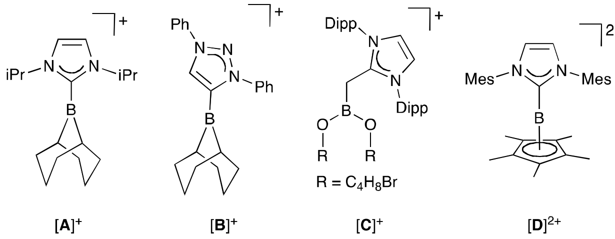
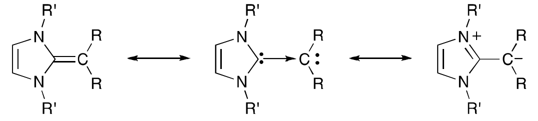


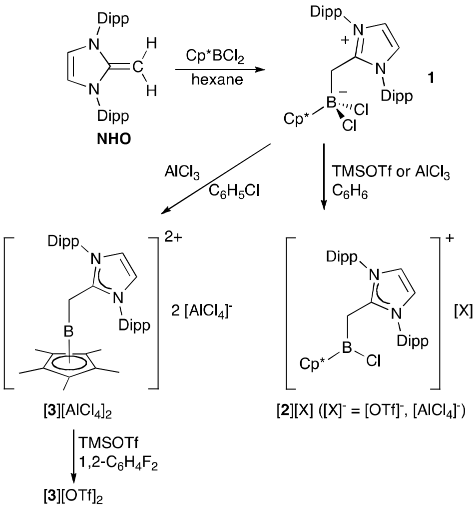
Figure 1: Examples of boron cations stabilized by carbon-based ligands.

Interestingly, the Cp*-coordinated NHC-stabilized boron dication ([**D**]$^{2+}$) was found to react with superhydride to afford the IMes-stabilized borabenzene.[24] To have a better understanding of dications featuring the hypercoordinated boron centre, we have prepared the related *N*-heterocyclic olefin (NHO) stabilized chloroborenium and boron dications and investigated their molecular electronics experimentally and computationally.



Scheme 1: Resonance structures of *N*-heterocyclic olefin.

The coordination of NHC to main group elements has shown to be critical in realizing highly reactive main group compounds.[25, 26] Recently, NHO ligand has also attracted much attention. Capping the ylidene carbon of NHC with a :CR_2 unit gives the so-called *N*-heterocyclic olefin (NHO), a strong σ-donating Lewis base.[27-33] The nucleophilic character of the methylene carbon of NHO can be explained with the ylidic resonance structure shown in Scheme 1. Sterically demanding NHO can be isolated and utilized as ligand for transition metals[28, 31, 32, 34, 35] and main-group Lewis acids.[36-39] Several NHO-coordinated boron derivatives have also been reported, such as di-alkoxylborenium cation (Fig. 1, [**C**]$^+$),[40] cationic hydrido boron derivatives,[41] borafluorene,[42] boranes,[29, 32, 43] and borylene intermediates.[44] As shown in the works of Rivard, NHO forms relatively weak E-C bond with main-group Lewis acids and can be readily replaced by DMAP and IPr.[42, 43] Theoretical computations also suggest that the coordination of NHO generally results in more electron deficient Lewis acidic centre than the related NHC analogues.[45] Thus, replacing the apical ligand of the Cp*-coordinated boron dication [**D**]$^{2+}$ from IMes to IPr=CH_2 (NHO) is expected to increase the reactivity of boron dication. Besides, the coordination of IPr=CH_2 generates a tetrahedral carbon centre that may impose steric congestion on the *nido*-$[C_5B]^{2+}$ moiety and leads to highly reactive boron dication.



Scheme 2: Synthesis of [**2**][X] and $[\mathbf{3}][X]_2$ ($[X]^-$ = $[AlCl_4]^-$ or $[OTf]^-$).

The NHO-Cp^*BCl_2 adduct (**1**) prepared from IPr=CH_2 and Cp^*BCl_2 was allowed to react with excess TMSOTf or $AlCl_3$ in benzene to yield the corresponding chloroboreniums ([**2**][X], $[X]^-$ = $[AlCl_4]^-$ or $[OTf]^-$) (Scheme 2). These two chloroboreniums feature identical ^1H NMR spectrum in CD_2Cl_2 implying the lack of counter cation-anion interaction in the solution. The methine hydrogen of NHO and the methyl groups of Cp* were respectively detected as sharp singlets at 2.26 ppm and 1.39 ppm. Unlike **1**, which features three distinct Cp*-Me signals at 1.96, 1.71, and 1.63 ppm, the presence of empty p orbital of borenium results in rapid sigmatropic rearrangement of $[\mathbf{2}]^+$ in the solution at room temperature.[46, 47] The detected ^{11}B resonance of $[\mathbf{2}]^+$ at 66.4 ppm is considerably down-field shifted compared to that determined for the related $[Cp^*BCl\text{-}L]^+$ cations (L = IMes (46.0 ppm),[24] acridine (32.8 ppm), phenanthridine (30.9 ppm)).[48]

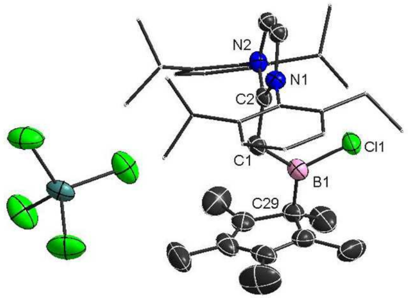


Figure 2: Molecular structure of [**2**][$AlCl_4$]. Hydrogen atoms and solvent molecule are omitted for clarity. Thermal ellipsoids are set at 50% probability level. Selected bond distances (Å) and angles (°): B1-C1 1.589(5), B1-Cl1 1.772(3), B1-C29 1.57(8), C1-C2 1.474(4), C1-B1-C29 125.0(10), Cl1-B1-C29 119.1(10), C1-B1-Cl1 115.8(2).

The absence of cation-anion interaction between $[\mathbf{2}]^+$ and counter anions has also been corroborated by single crystal X-ray diffraction analysis. In both cases, colourless single crystals were obtained from a saturated benzene solution of [**2**][X] at room temperature inside a glove box. As shown in Fig. 2, the boron atom of [**2**][$AlCl_4$] adopts a trigonal planar geometry with the sum of the bond angles around the boron atom of 359.9°. The B-Cl bond distance of 1.772(3) Å is comparable to that determined for chloroboreniums $[RBCl\text{-}L]^+$ (R = N(*i*-Pr)$_2$, L = IPr (1.787(3) Å);[26] R = acridane, L = acridine (1.757(5) Å)).[49] On the other hand, the B1-C1 distance (1.589(5) Å) is markedly longer than that observed in $[\mathbf{C}]^+$ (1.530(13) Å)[40] as a result of steric repulsion between NHO and Cp*. Compared with its IMes-coordinated analogue ([Cp*BCl-IMes][OTf]), which forms a cation-anion contact ion pair in solid state,[24] the lack of boron-triflate interaction in [**2**][OTf] suggests that IPr=CH_2 provides a better steric protection of the chloroborenium centre than IMes (Fig. S2).

To perform double chloride abstraction, compound **1** was mixed with four equivalents of $AlCl_3$ in chlorobenzene (Scheme 2). After stirring for 30 min at 80 °C, diethyl ether was introduced to wash away the excess $AlCl_3$ to afford $[\mathbf{3}][AlCl_4]_2$, which was then converted to $[\mathbf{3}][OTf]_2$ via the addition of TMSOTf to a 1,2-difluorobenzene suspension of $[\mathbf{3}][AlCl_4]_2$. The formation of the C_5B *nido*-carborane structure is verified by the detection of the highly shielded ^{11}B NMR signal at - 45.9 ppm in CD_3NO_2.[50-52] The aromatic ring current of Cp also results in highly up-field shifted ^{13}C resonance signal of the methine carbon of NHO (– 5.51 ppm). In the ^1H NMR spectrum of $[\mathbf{3}][OTf]_2$, Cp* was measured as a sharp singlet at 1.89 ppm and only one set of proton signals of the NHO was observed.

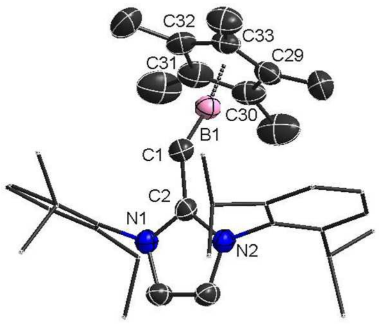


Figure 3: One of the independent molecules of $[\mathbf{3}][AlCl_4]_2$. Counter anions, solvent molecules and hydrogen atoms are omitted. Thermal ellipsoids are set at 50% probability level. Selected bond distances (Å) and angles (°): B1-C1 1.553(6), B1-C29 1.713(6), B1-C33 1.725(6), B1-C30 1.741(6), B1-C32 1.750(6), B1-C31 1.761(6), C1-C2 1.488(5), B1-C1-C2 126.4(3), C1-B1-$Cp^*_{centroid}$ 166.13.

The molecular structure of $[\mathbf{3}][AlCl_4]_2$ is further confirmed by X-ray diffraction analysis. Colourless crystals were obtained from slow cooling a saturated 1,2-difluorobenzene solution of $[\mathbf{3}][AlCl_4]_2$ from 80 °C to room temperature inside a glove box. $[\mathbf{3}][AlCl_4]_2$ crystallized as a difluorobenzene solvate in *P-1* space group with two independent molecules in the asymmetric cell. The two molecules are arbitrarily named **I** and **II**, and one of them is shown in Fig. 3 (molecule **I**). The $C_{(NHO)}$-B bond distance of 1.553(6) Å (**I**) and 1.568(6) Å (**II**) are shorter than that determined in $[\mathbf{2}\text{-}Cl]^+$ (1.589(5) Å), suggesting the presence of strong interaction between the lone pair of NHO and the radial empty sp orbital of boron centre. Interestingly, the $C_{(NHO)}$-B-Cp*$_{centroid}$ angles of 166.13° (**I**) and 160.53° (**II**) are considerably smaller than that observed in [Cp*B-IMes]$^{2+}$ (179.13°), leading to more distorted C_5B *nido*-carborane structure.

Preliminary reactivity studies of [**3**]$^{2+}$ show that [**3**]$^{2+}$ is considerably more reactive than its NHC-stabilized analogue, [**D**]$^{2+}$. While [**D**][$AlCl_4$]$_2$ is stable in nitromethane, [**3**][$AlCl_4$]$_2$ decomposes in nitromethane within 24 hours. To shed light on the reactivity differences between the NHC- and NHO-stabilized boron dications, theoretical calculations were carried out at the B3LYP/ 6-311G** level with applied nitromethane solvation using the polarisable continuum model (PCM).

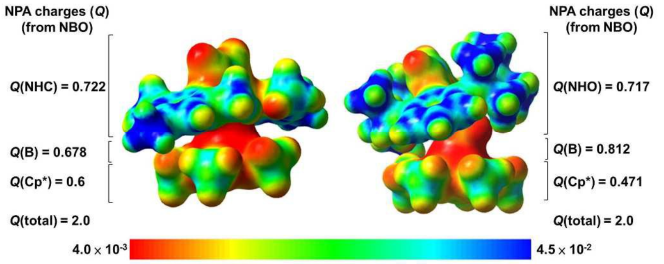


Figure 4: Electron potential surface of [**D**]$^{2+}$ (Left) and [**3**]$^{2+}$ (Right).

The optimised geometries of [**2**]$^{+}$, [**3**]$^{2+}$ and [**D**]$^{2+}$ are in good agreement with that determined experimentally. The linear and bent configuration of the [L-B-Cp*$_{centroid}$] moiety are respectively captured in the optimised structure of the NHC- and NHO-stabilized boron dications, showing that the structural distortion observed in the crystal data of [**3**]$^{2+}$ is not merely a result of crystal packing. As shown in Fig. 3, the electron deficient boron centres are well protected in both cases and the Cp* of [**D**]$^{2+}$ is slightly more electron positive than that of [**3**]$^{2+}$. The natural population analysis (NPA) reveals that considerable amount of positive charges are distributed over the apical ligand and the extent of charge transfer is nearly identical in both molecules (Fig. 4). Compared with the Q(B) value of 0.678 for [**D**]$^{2+}$, the boron centre of [**3**]$^{2+}$ (Q(B) = 0.812) bears more positive charges due to the lesser extent of charge transfer to Cp*. Thus, the instability of [**3**]$^{2+}$ is originated from to the steric repulsion between NHO and Cp* that diminishes the electron donation from the π-bonding orbitals of Cp* to the empty p orbitals of B^{2+} centre.

In order to differentiate the Lewis acidity of [**D**]$^{2+}$ and [**3**]$^{2+}$, the Gutmann-Beckett spectroscopic method was applied.[53] The changes in ^{31}P NMR chemical shift ($\Delta\delta$) between free Et_3PO in CD_3NO_2 and its Lewis acid adduct with [**D**]$^{2+}$, [**3**]$^{2+}$, and $B(C_6F_5)_3$ were found to be 1.9, 29.6, and 29.3 ppm, respectively. This result clearly indicates [**3**]$^{2+}$ has much higher Lewis acidity than that of [**D**]$^{2+}$. The same conclusion was also obtained from chloride ion affinity (CIA) calculation of [**D**]$^{2+}$ and [**3**]$^{2+}$.[10] As expected, the CIA of [**3**]$^{2+}$ (ΔH = 21.2 kcal/mol) is significantly greater than that of [**D**]$^{2+}$ (ΔH = 35.7 kcal/mol). The higher Lewis acidity of [**3**]$^{2+}$ is attributed to the presence of a more positively charged boron centre in [**3**]$^{2+}$ and the relief of steric congestion around the boron centre upon Lewis base coordination.

In conclusion, NHO-stabilized chloroborenium ([**2**][X]) and boron dications ([**3**][X]$_2$) have been prepared and characterized ([X] = [$AlCl_4$]$^{-}$ and [OTf]$^{-}$). The bent geometry of NHO significantly increases steric congestion at the boron centre, leading to the formation of a separated ion pair of [**2**][X] ([X] = [$AlCl_4$]$^{-}$ and [OTf]$^{-}$) in condensed phase. The steric repulsion between NHO and Cp* also renders [**3**]$^{2+}$ a stronger Lewis acid than its NHC analogue by reducing the charge delocalization from boron atom to Cp*. Applications of the reported boron mono- and dications in small molecule activation and ring-opening polymerization are currently under investigation.

This work is supported by the Ministry of Science and Technology of Taiwan (MOST 103-2113-M-002-005 and MOST 104-2113-M-002-018-MY3). Y.-F. Lin extends gratitude to MOST for a post doctoral fellowship (MOST 104-2811-M-002-130).

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details of **1**, [**2**][$AlCl_4$], [**2**][OTf], [**3**][$AlCl_4$]$_2$ and [**3**][OTf]$_2$. See DOI: 10.1039/c000000x/

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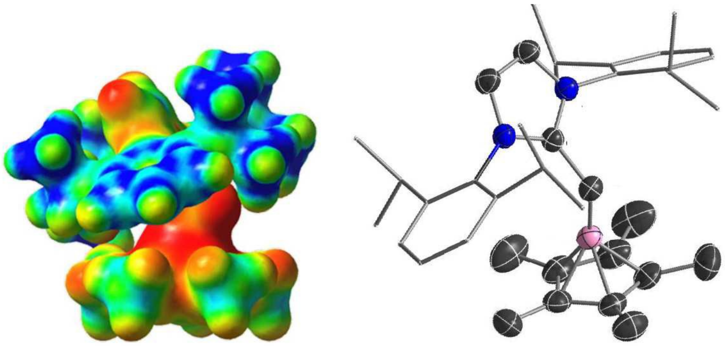

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